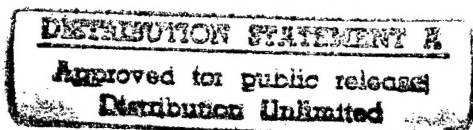UNITED STATES ATOMIC ENERGY COMMISSION

A GLASS STILL FOR THE EVALUATION OF
COLUMN PACKING WITH URANIUM
HEXAFLUORIDE

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A B S T R A C T

The operating holdup and flooding rates of uranium hexafluoride, n-heptane, and perfluorodimethylcyclohexane have been studied in a glass still filled with 1/8 inch nickel Heli-Pak. The flooding rates of the latter two substances are 46.0 and 48.0 cc./min. respectively and the flooding rate for uranium hexafluoride, calculated from the Bertetti equation, is 42.9 cc./min. The operating holdups for these three substances on Heli-Pak were measured at several throughput rates up to the flooding rate and an equation derived, based on the method of Jesser and Elgin, for computing the holdup of uranium hexafluoride from a knowledge of the holdup of perfluorodimethylcyclohexane. Observations of the performance of the packing and a measurement of the number of drops of uranium hexafluoride per milliliter at 75°C. are also presented.
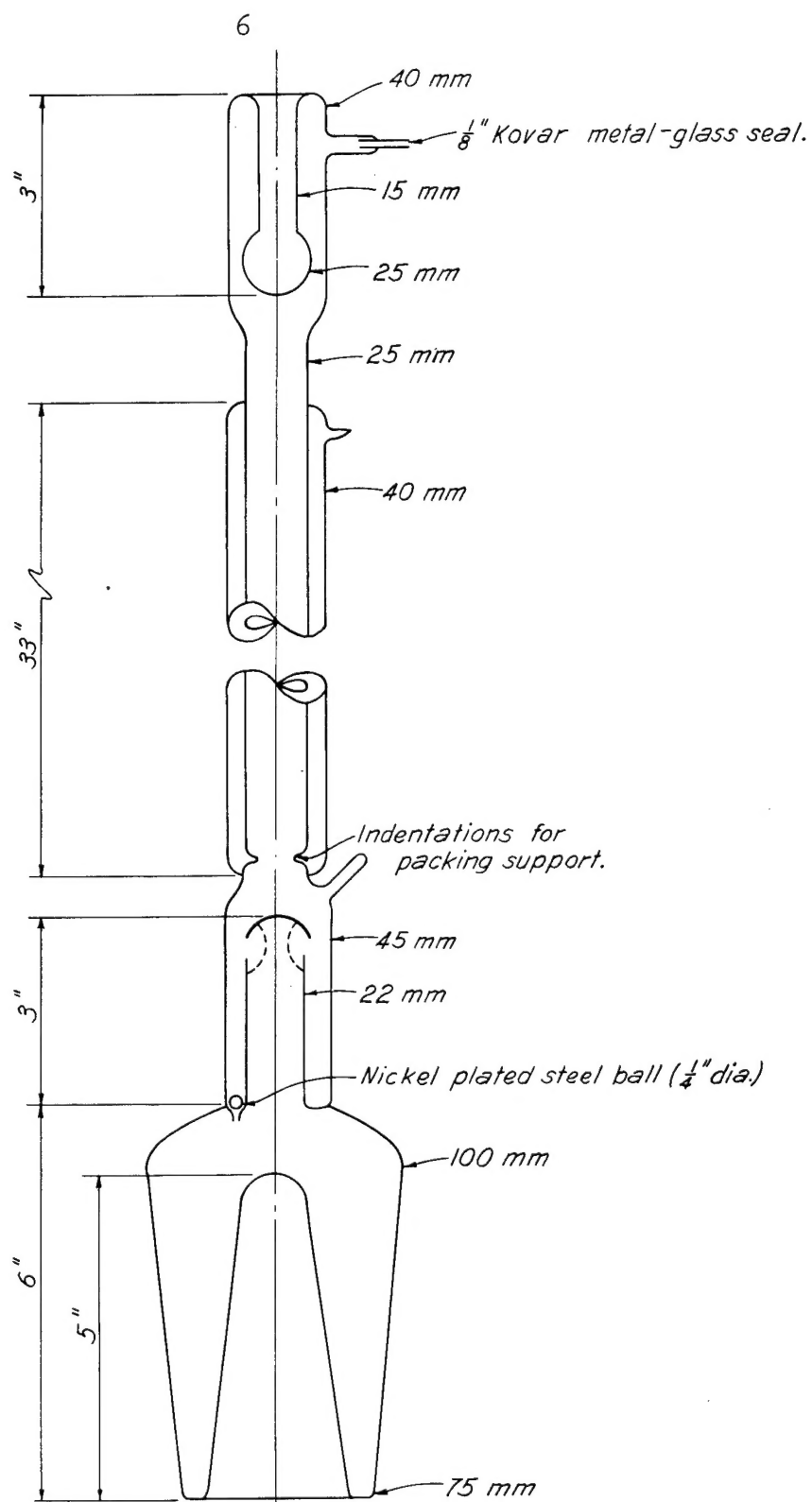
A GLASS STILL FOR THE EVALUATION OF COLUMN PACKING WITH URANIUM HEXAFLUORIDE

Recent studies of methods for the purification of uranium hexafluoride have demonstrated the need for a suitable procedure for the evaluation of the holdup and flooding characteristics of column packings used with uranium hexafluoride. Such information is of value in defining the operating conditions for the most efficient fractionation. Since direct measurements with uranium hexafluoride in a metal column are often impractical, the use of two inert calibrating fluids and uranium hexafluoride in a glass test column has been investigated and the results with the calibrating fluids related to uranium hexafluoride by means of the equations of Elgin and Jesser (4) and Bertetti (1). The present study is concerned with the evaluation of 1/8 inch nickel Heli-Pak in an 0.87 inch column. This packing, a product of Podbielniak, Inc., consists of 1/8 x 1/16 inch rectangular wire helices 1/8 inch long.

APPARATUS AND PROCEDURE

Equipment Design

A construction diagram of the glass still used in this study is shown in figure 1. Although the still was designed for operation under pressure, it was constructed throughout of standard wall pyrex tubing, heavy wall tubing being avoided because of its poorer resistance to thermal shock. The tapered construction of the pot was a safety measure to relieve the stresses developed by the expansion of solid uranium hexafluoride when heated. The upper section of the pot, the holdup volume, acted as a reflux separator. The vapors from the pot passed through the central tube into the column while the liquid reflux returned through the annular space between the central tube and the outside wall. A glass umbrella over the central tube prevented reflux from dripping directly into the pot. The pot was completed to the point of attachment of the vacuum jacketed column before calibration. The nickel plated steel ball was ground into its seat with fine abrasive to form a liquid tight seal. Calibration of the pot and holdup volumes at 75°C. was accomplished by immersing the pot in a constant temperature bath and pipetting distilled water into the proper volume. The liquid levels were then compared with linear scales which were later taped to the pot and holdup volumes. The column was a section of tubing chosen to closely approximate the inside diameter of 1 inch standard wall metal tubing, i.e. about 0.87 inch. The vacuum jacket was baked and pumped to a pressure of about 10^{-5} mm. of mercury and sealed off. A flat spiral grid of nickel wire resting on indentations at the bottom of the column was originally used as a packing support; however it was necessary to use a conical spiral with the hydrocarbon and fluorocarbon to prevent initiation of a flood at this point. The condenser was a simple cold finger type with an expanded tip to localize condensation. Prior to the attachment of the metal-glass seal to the condenser, the column was packed through the side arm with Podbielniak 1/8 inch nickel Heli-Pak. Some shaking was necessary to achieve compact arrangement. A total of 375 grams of Heli-Pak was used in the 32 inch packed section of the column, making a packing density of 11.7 grams/inch. No packing retainer was used at the top of the packed section. After final assembly, the entire still was hydraulically pressure tested to 60 psig.

6

40 mm

$\frac{1}{8}$" Kovar metal-glass seal.

15 mm

3"

25 mm

25 mm

40 mm

33"

Indentations for packing support.

45 mm

3"

22 mm

Nickel plated steel ball ($\frac{1}{4}$"dia.)

100 mm

6"

5"

75 mm

GLASS STILL
## (Construction details)

FIGURE I

A diagram of the still and its auxiliary equipment is shown in figure 2.
To enable the pot heat to be removed immediately, the pot heater was
mounted on the plunger of a hypodermic syringe which was connected by a
three-way stopcock to pressure or vacuum lines in order to raise or lower
the heater. A 110 volt electromagnet was mounted as shown to open or
close the ball valve in the holdup volume. A single switch was arranged
which would turn off the pot heater and electromagnet and open the solenoid
valve. Water was used as a coolant and was circulated from a dewar flask
by a small centrifugal pump. The still, gages, solenoid valve, nitrogen
ballast volume and uranium hexafluoride cylinder were mounted inside a
heated, thermostated transite box equipped with a door of 1/2 inch thick
Lucite. No heaters were mounted on the still in order to permit an un-
obstructed view of the packing.

Conditioning and Charging

Approximately 1700 grams of uranium hexafluoride was transferred to a
cylinder containing potassium fluoride which had been heated and dried in
vacuum. The uranium hexafluoride was melted at 80°C. and shaken to remove
hydrogen fluoride. An oil diffusion pump was attached to the assembled
still and allowed to pump overnight while the still box was heated to
120°C. The conditioning agent was admitted to the still to react with
adsorbed water. The reaction products were passed through the chemical
trap and the still again pumped overnight with the diffusion pump.
The box temperature was then lowered to 80°C. and the uranium hexa-
fluoride transferred vapor phase into the still pot which was cooled
to 65°C. with a water bath. It was not allowed to solidify in the
pot at any time. The material in the pot was a thin, pale yellow liquid
which boiled smoothly from the central cone. The coloration was also
present in the reflux, suggesting that it was not due to dissolved salts.
The still box was adjusted to 75°C. and sealed, all subsequent operations
being made outside the box.

Operation

The following procedure was used to obtain the required data with uranium
hexafluoride: With the ball valve open to return liquid to the pot, re-
flux was initiated by starting coolant to the condenser and heating the
pot. After a short reflux period, the still was lightly pumped to remove
any hydrogen fluoride driven into the condenser. The still was shut down
and the entire system allowed to reach thermal equilibrium. The column
was then pumped slowly to dry the packing. This could be verified by
observing the appearance of packing adjacent to the column wall viewed
tangentially. The volume of liquid in the pot was noted. Reflux was
again initiated by starting coolant flow and the pot heater adjusted to
maintain a desired reflux rate. After the rate had become constant, the
throughput rate was measured by shutting off the electromagnet to close
the ball valve and measuring the time required for a given volume of reflux
to collect. The ball valve was opened and the still allowed to reflux for
about thirty minutes. With the solenoid valve closed, nitrogen was admitted
to the ballast volume to a pressure 1 psi. above the column pressure. The
pot heater was lowered by applying vacuum to the syringe and the switch
thrown to close the ball valve and open the solenoid valve. The increased
column pressure immediately stopped ebullition in the pot. The coolant
was stopped and the system allowed to reach thermal equilibrium during
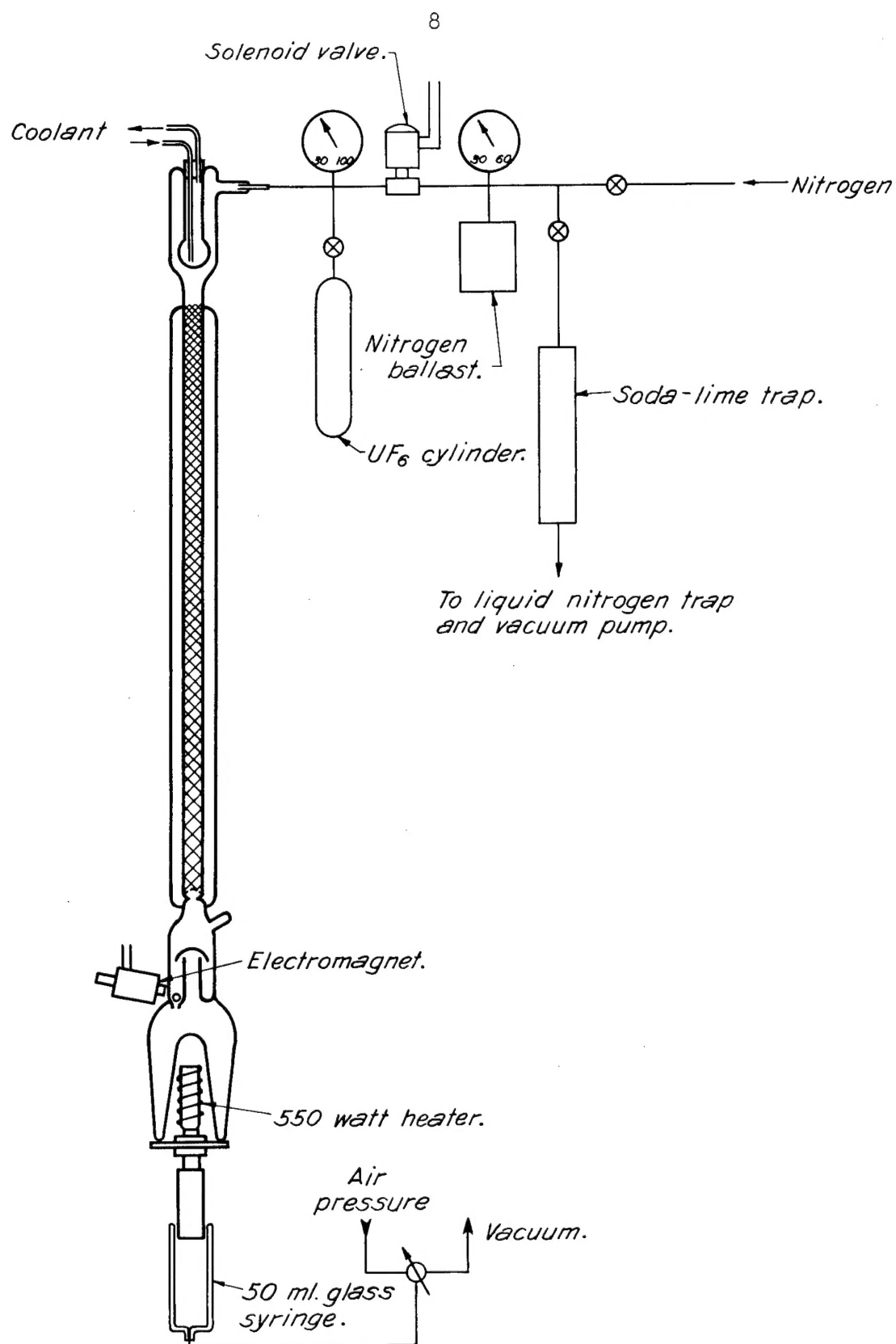
GLASS STILL WITH AUXILIARY EQUIPMENT

FIGURE 2

which time the liquid holdup drained into the holdup volume. The volumes
of holdup and pot were then noted. The column was again pumped to remove
nitrogen and dry the packing and measurements resumed at different through-
put rates.

Measurements of the drop volume of uranium hexafluoride were made by adjust-
ing the reflux rate to a rapid drip and counting the number of drops required
to fill the holdup volume to a specified level.

After all measurements with uranium hexafluoride had been completed, the still
was cleaned and examined for etching. Only a few clouded areas were found,
the largest being at the top of the condenser where hydrogen fluoride con-
centrated. A light deposit of uranyl fluoride covered the still but did not
obstruct vision.

The operating procedure was slightly modified for measurements using n-
heptane and perfluorodimethylcyclohexane (C_8F_{16}). Measurements with these
substances were made with the still open to the atmosphere, not under the
vapor pressure of the material as with uranium hexafluoride. Determination
of the flood rate was made by measuring the throughput rates at a series of
voltage settings on the pot heater until the flood point was reached.
Extrapolation of the rates to the voltage setting at which flooding started
gave the flood rate.

<div align="center">EXPERIMENTAL RESULTS</div>
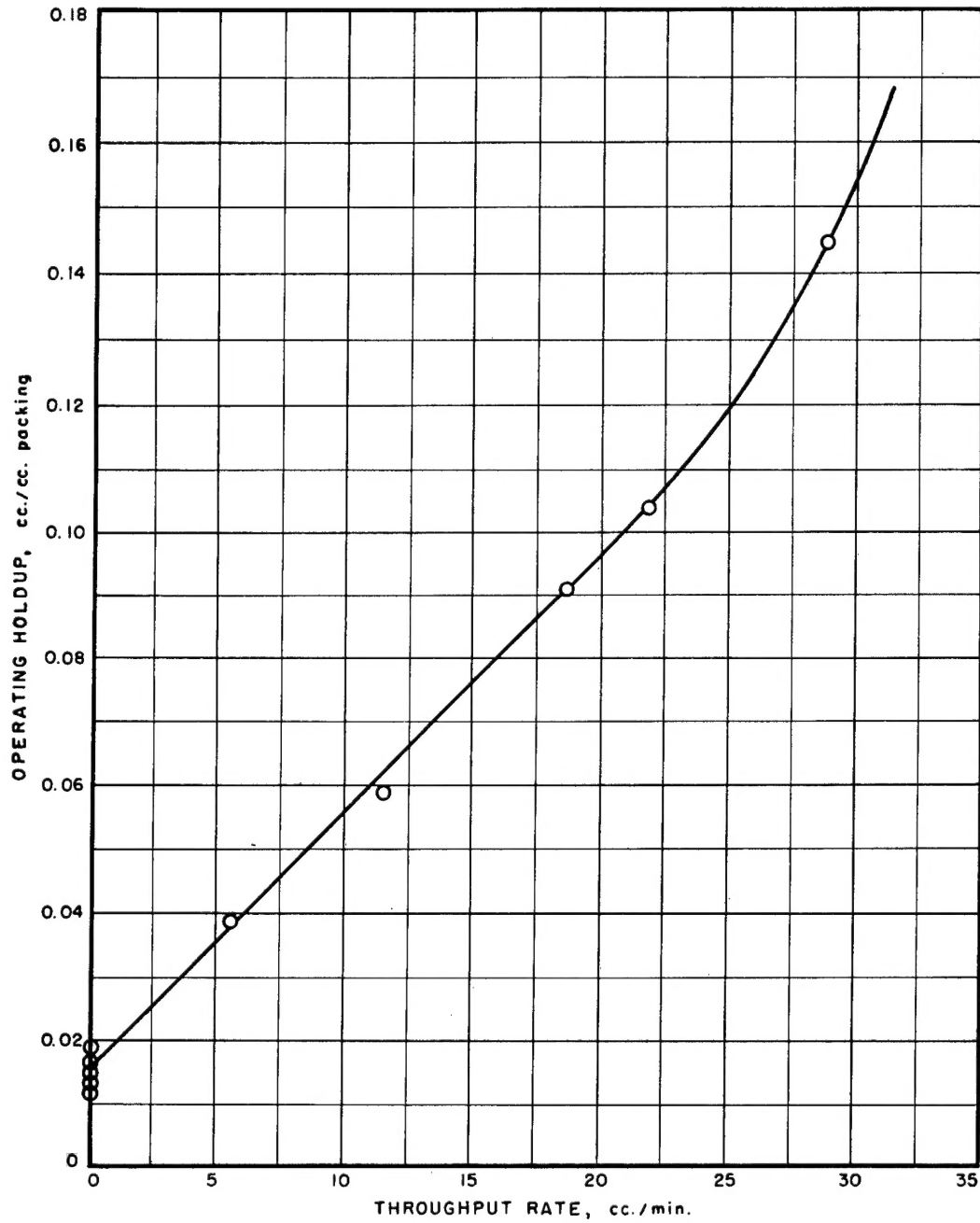
Packing Holdup

The liquid holdup in a packed column is expressed in the following manner:

    (1) The operating holdup, consisting of all liquid above the surface
of the liquid in the pot.
    (2) The dynamic holdup, consisting of that fraction of the operating
holdup which can be drained from the column. It is this holdup which in-
creases with increasing throughput.
    (3) The static holdup, consisting of the amount of material necessary
to wet the packing and column walls.

These quantities were obtained from the measurements described above as
follows: The operating holdup was taken as the difference in the volume of
material in the pot before reflux started and after the system had returned
to thermal equilibrium. The dynamic holdup was measured directly as the
volume of material which drained from the column into the holdup volume.
The static holdup was then calculated as the difference between the operating
and dynamic holdup. These values for the three substances studied are sum-
marized in table I and shown graphically in figures 3, 4, and 5 as the holdup
per cubic centimeter of packing. In these figures the static holdup is plotted
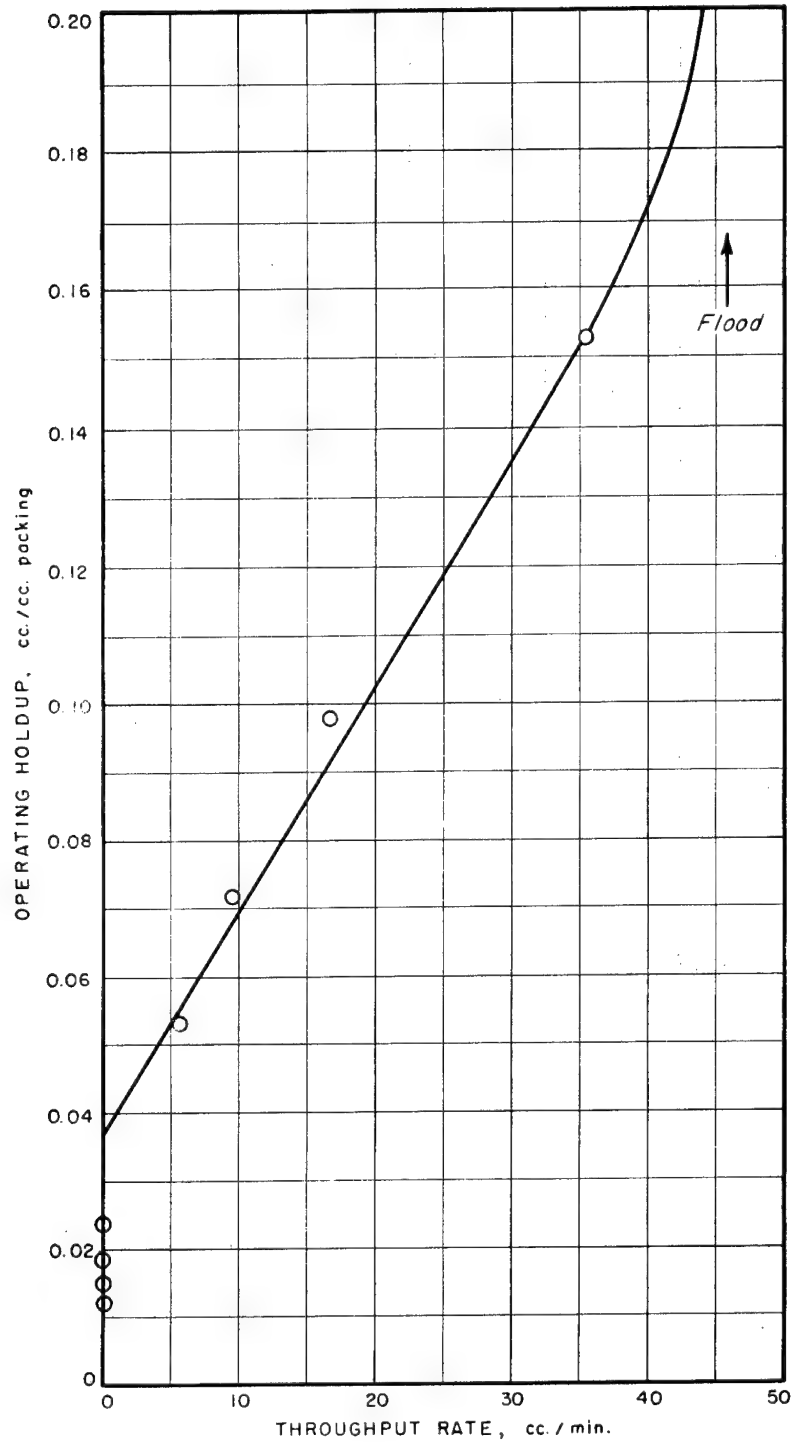as the operating holdup at zero throughput.

UF$_6$

OPERATING HOLDUP ON 1/8" HELI-PAK

FIGURE 3
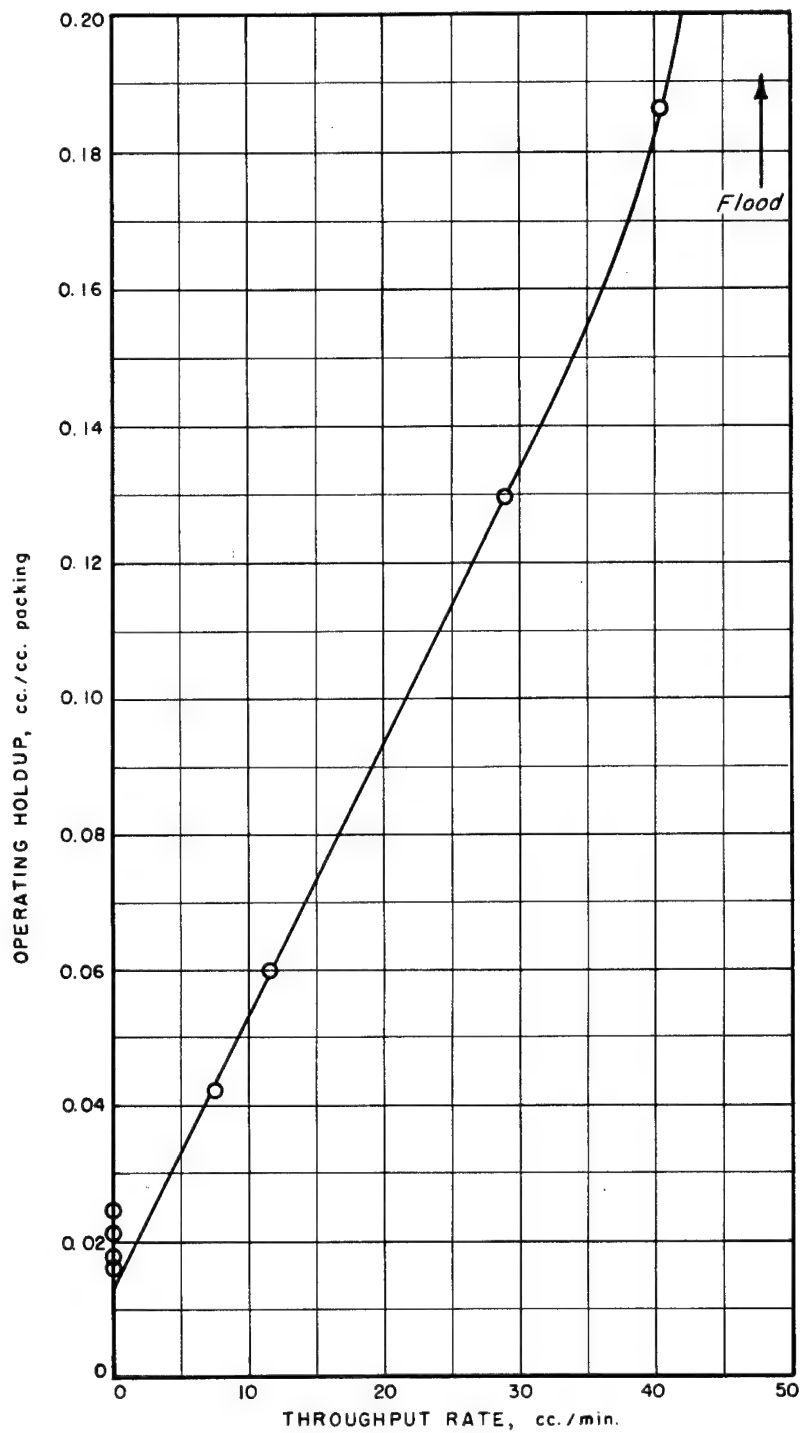
C₈F₁₆

OPERATING HOLDUP ON 1/8" HELI-PAK

FIGURE 4

n - HEPTANE
OPERATING HOLDUP ON 1/8" HELI-PAK

FIGURE 5

TABLE I

LIQUID HOLDUP IN PACKED COLUMN

Column: 22 mm. I.D., 32 inches long
Packing: 1/8 inch nickel Heli-Pak, 11.7 grams/inch

Material	Throughput, cc/min liquid	Operating Holdup, cc.	Dynamic Holdup, cc.	Static Holdup, cc.
Uranium	5.64	12.0	8.0	4.0
Hexafluoride	11.55	18.0	13.2	4.8
	18.80	28.0	22.0	6.0
	22.00	32.0	27.0	5.0
	29.00	44.5	40.0	4.5
n-Heptane	5.69	16.5	12.0	4.5
	9.44	22.0	18.5	3.5
	16.85	30.0	23.0	7.0
	35.50	47.0	41.5	5.5
C_8F_{16}	7.46	13.0	7.0	6.0
	11.30	18.5	11.0	7.5
	29.00	40.0	33.5	6.5
	40.50	57.5	51.5	6.0

Several unsuccessful attempts were made to obtain the flood rate using uranium hexafluoride. It was found that the flood rate exceeded the capacity of the short condenser and the condensation ring rose into the side arm. Lowering the coolant temperature resulted in the solidification of uranium hexafluoride at the top of the cold finger which made throughput and holdup measurements impossible. Hence, the uranium hexafluoride flood rate has been calculated from physical constants and is discussed in the next section. The flood rates for n-heptane and perfluorodimethylcyclohexane were obtained as previously described and were found to be 46.0 and 48.0 cc./min. respectively.

In addition to the holdup measurements made with uranium hexafluoride, the number of drops per milliliter was determined. An average of two drop counts gave a value of 117 drops/ml. at 75°C. An examination of the technique employed suggests that the values are biased low since any material condensing on the outer wall of the condenser or in the column increases the volume of material measured without increasing the drop count. While this fact made it unfeasible to use the same technique with n-heptane and perfluorodimethyl-cyclohexane, there was no visible condensation ring on the outer wall with uranium hexafluoride and it is felt that the value stated is of a magnitude consistent with the density and surface tension of uranium hexafluoride.

DISCUSSION OF RESULTS

The equation developed by Bertetti (1) for the calculation of the flooding velocity in packed columns is as follows:

$$K = 4.85\,\mu^{0.04}R^{1/3}U_g^{2/3} + 4.1\,\mu^{0.10}U_1^{2/3} \qquad (1)$$

where
K = Flooding velocity constant
μ = Viscosity of liquid in centipoises
R = Ratio, density of gas/density of liquid
U_g = Superficial gas velocity in feet per second
U_1 = Superficial liquid velocity in feet per second

The constant K was determined by measuring the flooding velocity of n-heptane and perfluorodimethylcyclohexane (C_8F_{16}) in the column and substituting in equation 1. The physical constants used and results obtained are summarized in table II.

TABLE II

EVALUATION OF $\underline{K}$ FROM OBSERVED FLOOD RATES

Material	Flood Rate, cc./min.	T, °C.	Viscosity, centipoises	R	U_g, ft./sec.	U_1, ft./sec.	K
n-Heptane (4)	46.0	98	0.2096	0.0052	1.271	0.00662	1.050
C_8F_{16} (5)	48.0	101	0.5110	0.0078	0.883	0.00690	1.002
						Avg.	1.026

For this packing and column diameter, equation 1 may be written

$$U_1 = \left(\frac{1.026}{4.1\,\mu^{0.1} + 4.85\,\mu^{0.04}/R^{1/3}} \right)^{3/2} \qquad (2)$$

since at total reflux $U_g = U_1/R$. Using equation 2 and the proper physical constants of uranium hexafluoride (5) at 75°C. (μ = 0.663 cp, R = 0.00581), the flooding velocity for uranium hexafluoride was found to be 42.9 cc./min. The highest velocity attained with uranium hexafluoride in the still was about 30 cc./min. The flooding velocity may also be estimated by the method of Sherwood, Shipley, and Holloway (6), although certain information necessary for the use of their relationship was not available for the packing used.

The holdup values shown in figures 3, 4, and 5 should be applicable to

columns of any length and diameter. The information presented in these curves may also be expressed mathematically by a modification of the equation of Jesser and Elgin (4). The holdup (H_a) should be related to the holdup of a calibrating fluid (H_b) in the following manner:

$$H_a = H_b \frac{\mu^{0.10}}{\rho^{0.78} \sigma^n} \tag{3}$$

where μ = Relative viscosities, μ_a/μ_b

ρ = Relative densities, ρ_a/ρ_b

σ = Relative surface tensions, σ_a/σ_b

n = Surface tension exponent

Substituting the values of μ, ρ, and σ for uranium hexafluoride (a) and perfluorodimethylcyclohexane (b) in equation (3) reduces it to a form

$$H_a = H_b \frac{C}{(1.722)^n} \tag{4}$$

The surface tension exponent n varies with the throughput rate. Taking C = 0.80, the values of n observed at various mass throughput rates for these substances are shown in figure 6. It should be emphasized that these values are based on measurements with uranium hexafluoride and perfluorodimethylcyclohexane only.

Within the experimental error , the static holdup was found to be essentially independent of the material refluxed.

Examination of the packing at different throughput rates indicated that a large fraction of the reflux flowed down the column walls at low rates (~5 cc./min.) and there was some doubt as to whether the packing in the center of the column was being wet. At high throughput rates, particularly close to the flooding rate, the packing appeared uniformly wet and the fraction flowing down the walls appeared to decrease.

The flooding characteristics of Heli-Pak seem to be excellent. The use of flat packing supports at the bottom of the column should be avoided unless the diameter of the column is increased at this point since the resulting constriction causes flooding to start prematurely. A conical support eliminated this effect completely. The floods referred to in the present study all started at the top of the packing.

SUMMARY

The holdup and flooding rates of uranium hexafluoride, n-heptane, and perfluorodimethylcyclohexane have been studied in a glass still filled with 1/8 inch nickel Heli-Pak. The packed section of the column was 0.87 inch inside diameter and 32 inches long. The flooding rates of the latter two substances are 46.0 and 48.0 cc./min. respectively and the flooding rate for uranium hexafluoride, calculated from the Bertetti equation, is 42.9 cc./min. The operating holdups for these three substances on Heli-Pak were measured at several throughput rates up to the flooding rate and an equation derived, based on the method of Jesser and Elgin, for computing the operating
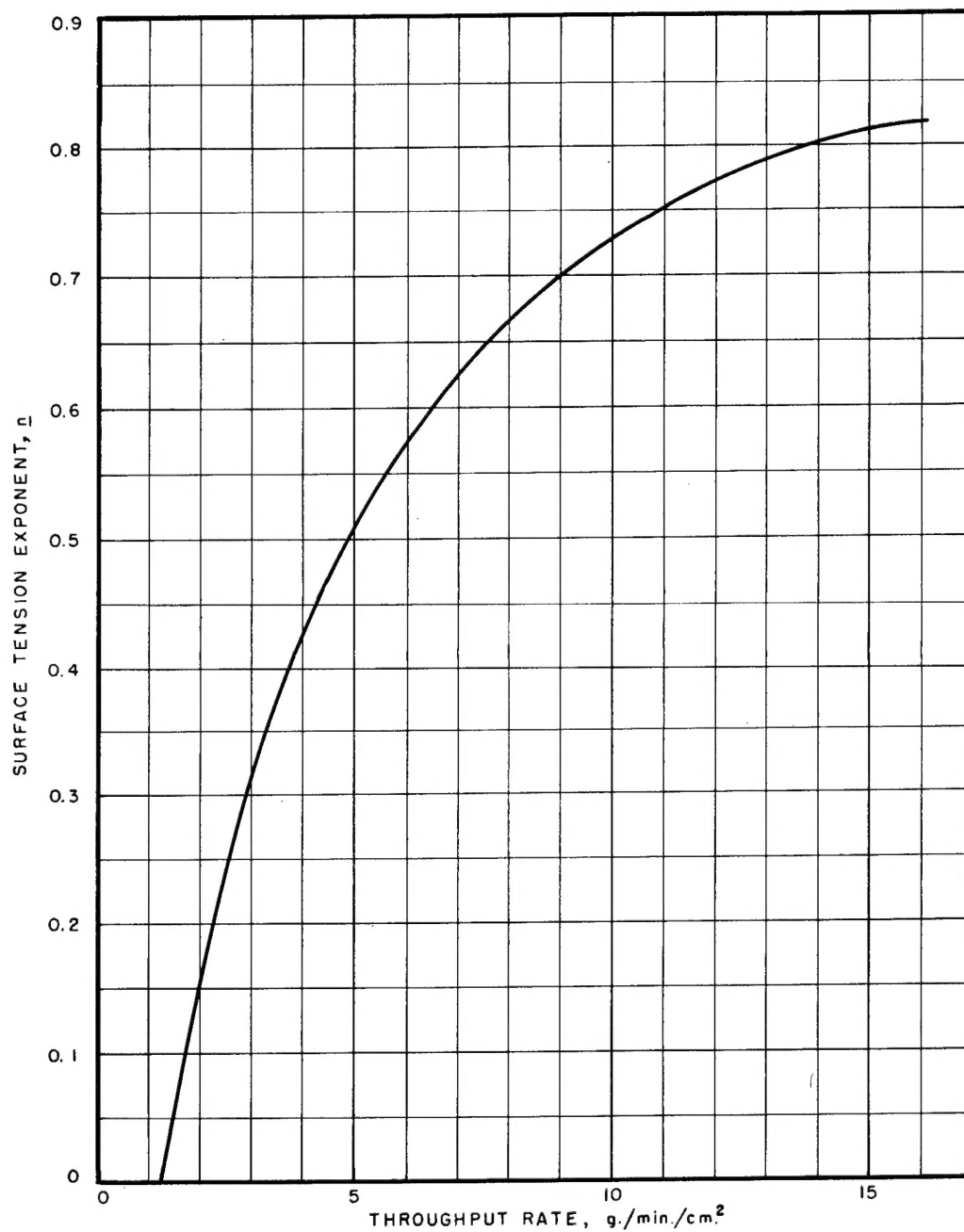
EVALUATION OF SURFACE TENSION EXPONENT

FIGURE 6

holdup of uranium hexafluoride from a knowledge of the holdup of perfluorodimethylcyclohexane. Observations of the performance of the packing at different throughput rates and a measurement of the number of drops of uranium hexafluoride per milliliter at 75°C. are also presented.

ACKNOWLEDGEMENTS

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